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CELLULOSE NITRATION

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This invention relates to the nitration of cellulose and to the product so produced. In a specific aspect this invention relates to an improved process for nitrating a cellulosic material to produce a uniformly nitrated high viscosity nitrocellulose.

Nitrocellulose of different types is used commercially in protective coatings, films, plastics, dynamite, and smokeless powder. For all practical purposes, the lower limit of the nitrogen content in nitrocellulose that is presently used commercially is 10.5%, and the upper limit of the nitrogen content is about 13.8%. The nitrocellulose that is used in the nonexplosives fields is generally referred to as soluble nitrocellulose, and it differs from the type of nitrocellulose used in explosives in that the nitrogen content of the former is lower than about 12.3%.

In present commercial practice, nitrocellulose is produced by nitration of cellulosic material with a nitration mixture containing sulfuric acid, nitric acid, and water. The sulfuric acid is not consumed in the nitration reaction, and this acid must be handled and reconcentrated in expensive equipment because of its extremely corrosive nature at elevated temperatures. Since the sulfuric acid forms the bulk, say more than 50%, of the nitration mixture, there is a considerable quantity of such acid to be handled in this type of process. Also, the nitrocellulose resulting from the process contains from 1 to 2 lb. of nitrating mixture per lb. of product, and this retained mixture cannot be recovered readily because its heat of dilution with water causes denitration of the nitrocellulose product. Further, in such a nitration procedure the sulfuric acid tends to form sulfate esters of cellulose which are undesirable in the product because they cause low heat stability of the nitrocellulose product. Consequently, it is necessary to give the product a long acid boil to hydrolyze off the undesirable sulfate groups. Additionally, when nitrating with such a nitration mixture, the cellulose is degraded to varying degrees depending upon the temperature, oxide content, mechanical handling, and water content of the mixture. This degradation causes a sharp reduction in viscosity of the final product.

Prior to this invention it was known that cellulosic material could be nitrated with mixtures of nitric acid and water, but the nitration process presented problems which heretofore were not solved in such a manner that the process was regarded of commercial importance. Nitric acid-water mixtures containing less than about 75% nitric acid were found to be ineffective for nitrating cellulose. Mixtures containing from 75% to about 89% nitric acid seriously swell or completely dissolve the cellulosic material without effectively esterifying it. Mixtures containing more than 89% nitric acid are known to esterify cellulose, but the rate of reaction at normal temperatures is uncontrollably rapid resulting in incomplete penetration of the cellulose fibers and a harsh, nonuniform nitration product. Consequently, it is an object of this invention to provide an effective procedure for nitrating cellulose with mixtures of nitric acid and water in a process that eliminates the difficulties and problems of prior art procedures.

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It is an object of this invention to provide a novel and improved process for nitrating cellulosic material.

It is another object of this invention to provide a novel and improved process for nitrating cellulosic material with aqueous nitric acid solutions.

It is another object of this invention to produce a high viscosity, uniformly nitrated nitrocellulose which is stable without the long purification boiling treatment employed in commercial operations.

Further and additional objects and advantages of this invention will be apparent from the detailed disclosure set forth hereinbelow.

The difficulties of the prior art are overcome, and the objects and advantages of this invention are achieved by nitrating a cellulosic material with a concentrated aqueous solution of nitric acid in a two-step process. In the first step a partial nitration of the cellulose is effected at a temperature lower than the temperatures normally employed in the nitration of cellulose and at which substantially no dissolution and/or swelling of the cellulose takes place. The resulting partially nitrated cellulose is then further nitrated with a concentrated aqueous solution of nitric acid at a temperature higher than the temperature employed in the first step. The resulting product is a nitrocellulose of high viscosity and uniform nitration and stable without the long purification boiling treatment normally employed.

The following examples are illustrative of various aspects of this invention and of the advantages of employing the two-step nitration procedure.

Example 1

Thin sheeted filter paper was prepared for nitration by cutting into small strips approximately 1½ inches by ½ inch, crimping and drying for one hour at 105° C. Three grams of the dry cellulose and 100 ml. of nitric acid having a concentration of 91.27% were mixed in a beaker by adding the dry cellulose to the acid with stirring. The temperature of the mixture was maintained at 30° C. for 20 minutes. The acid was then drained off and the nitrated cellulose was drowned in a large excess of water. The result-

ing nitrated cellulose was insoluble in acetone indicating nonuniform nitration, and the product was harsh indicating a swelling and softening of also was harsh indicating a swelling and softening of the cellulose fibers with subsequent hardening thereof and a gelation of nitrated cellulose in the nitric acid.

Example 2

The procedure described in Example 1 was employed using nitric acid having a concentration of 95.82%. The temperature of the mixture was maintained at —30° C. by employing a bath of Dry Ice in acetone, and the contact time was 10 minutes. The nitrated product contained 12.34% nitrogen. The nitrocellulose was insoluble in acetone and it was also harsh.

Examples 3–13

A series of runs was made in which a two-step nitration procedure was employed. In each of these runs 2 grams per 100 ml. of acid were used. The pertinent conditions in each of the two steps and the properties of the resulting nitrocellulose product are set forth in the table below.

Examples	First Step			Second Step				Solubility of the Product in Acetone	Remarks
	Percent HNO_3	Temp., ° C.	Time in Min.	Percent HNO_3	Temp., ° C.	Time in Min.	Percent N_2		
3	94.60	—6	10	94.60	41	10	13.40	Soluble	Slight harshness.
4	94.60	—6	10	91.75	41	10	12.90	do	Very slight harshness.
5	91.27	0	10	91.27	41	10	12.60	do	Do.
6	91.22	—5	10	91.22	41	10	12.35	do	Soft.
7	90.45	0	10	90.45	40	10	12.16	do	Do.
8	90.45	0	10	90.45	40	30	12.01	do	Do.
9	90.45	0	10	92.45	40	10	12.37	do	Do.
10	92.17	—5 to 0	20	98.57	40	20	13.41	do	
11	93.95	—5 to 0	20	95.00	40	20	13.29	do	
12	93.95	—5 to 0	20	95.00	40	20	13.30	do	
13	93.95	—5 to 0	20	98.57	40	20	13.26	do	

The process of this invention is a two-step procedure wherein a partial nitration of the cellulose is effected in the first step. The nitrating conditions are such that the cellulose is substantially undissolved in and unswollen by the nitrating mixture, and in this step a slow rate of nitration is desired in order to prevent excessive dilution of the nitric acid in contact with and within the cellulose and partially nitrated cellulose fibers by water formed during the nitration reaction. In the second step the partially nitrated cellulose is further nitrated in a bath at a temperature higher than that employed in the first step. After the desired level of nitration is attained, the product is washed in cold water to remove excess acid, and the resulting product is soft, soluble in acetone and thermally stable without acid boiling.

The nitrating acid for the first step has a concentration suitable for nitrating the cellulosic material without substantial swelling or dissolution of the cellulose, and it is preferably limited to a range of 89 to 95 weight per cent. At concentrations lower than 89% the nitric acid tends to swell and dissolve the cellulosic material. In some instances concentrations above 95% can be used, but at such concentrations the nitration reaction tends to become too rapid resulting in a harsh nonuniformly nitrated product. The temperature employed in the first nitration step is generally within the range of —50° to 10° C., and the preferred temperature is within the range of —20° to 0° C. The optimum temperature for this step is within the range of —10° to 0° C. Temperatures below —10° C. are operable, but the reaction rate is slowed to a point where longer contact times are necessary to reach the desired degree of nitration. At temperatures above 10° C. the nitration reaction is rapid enough to cause harshening of the product and nonuniform nitration.

To prevent partial dissolution of the nitrocellulose in the second step of the process, a nitrogen level of at least 9% is achieved in the first or partial nitration step. The preferred minimum nitrogen level for the product of the first step is 9.5%, but the maximum level of nitration varies with the type of nitrocellulose being produced. If a soluble type of nitrocellulose is being produced, the product from the first step contains no more than about 10.5% nitrogen, and, if nitrocellulose is being produced for use in explosives, the product from the first step can, in some instances, contain as much as 13% nitrogen. The nitrogen level of the first step product should be substantially below the nitrogen level desired in the finished product in order to obtain uniformity of nitration in the final product of the process. If the minimum level of nitration is not attained in the first step for reasons such as too weak a nitrating acid, too low a reaction temperature, or too short a contact time, a uniform nitration is not obtained in the second step of the process. In general, the desired level of nitration in the first step can be attained at a contact time within the range of 5 to 60 minutes. Ordinarily, the concentration of the nitrating acid and the reaction temperature are such that the desired level of nitration is attained in the preferred time range of 10 to 20 minutes.

After nitration in the first bath at reduced temperature has proceeded to the degree necessary to prevent a dissolving action in the nitric acid at a higher temperature in the second step, the partially nitrated nitrocellulose from the first step is ready for further nitration at a higher temperature. Various means are available for accomplishing this second nitration step. For example, the partially nitrated nitrocellulose can be retained in the first bath which is then adjusted by the addition of nitric acid thereto in order to obtain the desired nitric acid concentration. The bath is then heated to a suitable temperature for effecting the second nitration step, and the bath is maintained at that level for the desired period of time. Alternatively, the partially nitrated nitrocellulose can be removed from the first bath and passed to a second nitrating bath having the necessary nitric acid concentration and temperature level. It is thus apparent that various alternative procedures are available for accomplishing the second step of the nitration process.

The nitric acid concentration in the second nitration step is generally within the range of 90

to about 99 weight per cent, and the temperature at which this nitration reaction is effected is generally above that employed in the partial nitration step and within the range of 10° to 45° C. Since the uniformity of the reaction in the second step is enhanced by higher temperatures (nitration at 40° C. being superior to nitration at 20° C.), the preferred temperature for the second step is within the range of 30° to 40° C. The contact time employed in the second step is within the range of 10 to 60 minutes and preferably within the range of 20 to 30 minutes.

In this nitrating process any suitable cellulosic material from cotton, wood fiber, straw, or other source, can be used. The cellulose can be in any suitable form for nitration, such as a bulk or shredded form. The primary purpose of the use of a low temperature for the initial step of the process is to lower the nitration reaction rate and thus to inhibit or eliminate the dissolving effect of nitric acid diluted by water of reaction. To achieve this purpose it is advantageous to have the cellulosic material in a dense physical form, since the dense nature of the material aids in retarding the partial nitration reaction rate and in resisting the dissolving effect of the nitric acid. It is desirable to use a cellulosic material not in a finely-divided form, and it is preferred that the material to be nitrated be in a dense, sheet form. In each step of the process the ratio in parts by weight of cellulosic material to nitric acid solution is ordinarily within the range of 1:30 to 1:75.

In a specific aspect the nitration process can be carried out by employing a roll of cellulosic material, such as cotton linters and the like. The cellulose is unrolled in sheet form and passed through the first nitration bath at a temperature and a speed effective for accomplishing the necessary partial nitration. The sheet of partially nitrated cellulose can then be passed through squeeze rolls to remove excess acid, but in some instances it can be passed directly to the second nitration step where it is further nitrated. After the second nitration step, excess acid is removed from the sheet of nitrocellulose which is then washed with water to remove remaining acid. The resulting sheet of nitrocellulose if desired, can be shredded or otherwise comminuted prior to passage to a digestion step.

Since the nitrating acid for the final nitrating step can have a concentration higher than the concentration of the nitric acid for the partial nitration step, this invention is readily adaptable to a countercurrent nitration process. In such a process concentrated nitric acid is introduced to the second nitration step where it is used to nitrate partially nitrated cellulose from the initial step of the process. The nitric acid is diluted by water of reaction, and, after passage through refrigeration means, it is passed to the initial partial nitrating step to nitrate the feed cellulosic material. Nitric acid from the partial nitration step is then reconcentrated by any suitable method and then recycled to the second nitration step.

In another embodiment countercurrent nitration can be achieved in accordance with this invention by passing the cellulosic material through a tube or conduit provided with conveying mechanism, such as a screw conveyor. Concentrated nitric acid is passed, either by gravity or by pumping, through the conduit countercurrent to the flow of cellulose. The conduit is suitably jacketed to provide the necessary heating and cooling in order that the temperature levels for partial and final nitration can be maintained.

From the above disclosure various modifications within the scope of the invention will be apparent to those skilled in the art.

What I claim and desire to protect by Letters Patent is:

1. The method of producing a uniformly nitrated nitrocellulose which comprises partially nitrating a cellulosic material with an aqueous nitric acid solution at a temperature not substantially above 10° C., and further nitrating thus partially nitrated cellulosic material with an aqueous nitric acid solution at a temperature higher than the first-named temperature and not substantially below 10° C.

2. The method of producing a uniformly nitrated nitrocellulose which comprises partially nitrating a cellulosic material with an aqueous nitric acid solution containing at least 89 weight per cent nitric acid at a temperature within the range of −50° to 10° C., and further nitrating thus partially nitrated cellulosic material with an aqueous nitric acid solution containing from 90 to 99 weight per cent nitric acid at a temperature above the first-named temperature and within the range of 10° to 45° C.

3. The method of producing a uniform nitrocellulose which comprises partially nitrating a cellulosic material with an aqueous nitric acid solution containing from 89 to 95 weight per cent nitric acid at a temperature within the range of −20° to 0° C. for a period of time within the range of 5 to 60 minutes, and further nitrating thus partially nitrated cellulosic material with an aqueous nitric acid solution containing from 90 to 99 weight per cent nitric acid at a temperature within the range of 30° to 40° C. for a period of time within the range of 10 to 60 minutes.

4. The method according to claim 3 wherein the partial nitration step is effected for a period of time within the range of 10 to 20 minutes and until the nitrated cellulose contains at least 9% nitrogen.

5. The method according to claim 3 wherein the partially nitrated cellulosic material is further nitrated for a period of time within the range of 20 to 30 minutes.

6. The method of partially nitrating a cellulosic material which comprises contacting said solution containing at least 89 weight per cent nitric acid at a temperature within the range of −50° to 10° C. and for a period of time within the range of 5 to 60 minutes.

7. The method of partially nitrating a cellulosic material which comprises contacting said cellulosic material with an aqueous nitric acid solution containing from 89 to 95 weight per cent nitric acid at a temperature within the range of −20° to 0° C. for a period of time within the range of 10 to 20 minutes and until the nitrated cellulose contains at least 9% nitrogen.

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